KINETICS OF THE REACTION BETWEEN MAGNESIUM OXIDE AND AMMONIUM CHLORIDE SOLUTION

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The kinetics of the reaction between magnesium oxide and ammonium chloride solution in a well-stirred batch reactor have been investigated. The results have shown that the rate-controlling step is the dissolution of the solid phase. A kinetic equation has been derived for this variant of reaction mechanism.

In the Solvay process of making soda ash, $CaCl_2$ forms as an undesired by-product. One way to avoid its formation is to replace lime milk used to recover ammonia from the filter liquor by magnesium oxide obtained by heat treatment of magnesite. During the reaction, magnesium passes to solution together with a small amount of calcium, but the latter can be removed by incorporating a purifying operation. The resulting solution of magnesium chloride with an admixture of sodium chloride is sufficiently pure to permit the processing to very pure MgO or other magnesium compounds. There are, however, no kinetic data available to assess the commercial feasibility of the reaction under consideration.
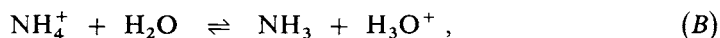
THEORETICAL
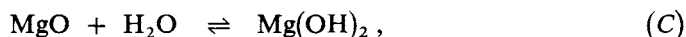
The reaction can be described by the stoichiometric equation

$$2\,NH_4Cl + MgO = MgCl_2 + 2\,NH_3 + H_2O^{\bullet} \qquad (A)$$
$$2\,A + B = X + 2\,Y + Z$$
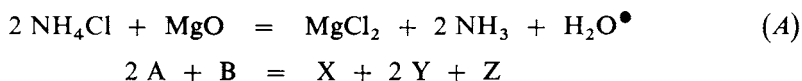
From the macrokinetic point of view, the reaction involves three chemical processes:

1. NH_4Cl hydrolysis

$$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+, \qquad (B)$$

2. MgO hydration

$$MgO + H_2O \rightleftharpoons Mg(OH)_2, \qquad (C)$$

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3. neutralization of H_3O^+ by OH^- ions

$$H_3O^+ + OH^- \rightleftharpoons 2\,H_2O, \qquad (D)$$
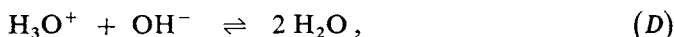
and the following physical processes:

4. desorption of NH_3 from the solution,
5. dissolution of $Mg(OH)_2$,
6. transfer of H_3O^+ ions from the bulk of the liquid to the interface by a) outer diffusion, and b) inner diffusion,
7. transfer of OH^- ions from the interface to the bulk of the liquid by a) inner diffusion, and b) outer diffusion,
8. transfer of Mg^{2+} ions from the interface to the bulk of the liquid by a) inner diffusion, and b) outer diffusion.

If the mechanism of MgO hydration presented in the literature[1-5] is considered, then processes 2 and 5 are replaced by MgO dissolution. The rate of removal of substance B (MgO) per unit volume of reactor, r_{BV}, is defined as

$$r_{BV} = -(1/V)(dn_B/d\tau) = S_V r_{BS}, \qquad (1)$$

where r_{BV} is in the units mol m^{-3} s^{-1}, r_{BS} is the reaction rate per unit MgO surface area, mol m^{-2} s^{-1}, V is the reactor volume, m^3, n_B is the number of moles of MgO in the reactor, mol, τ is the reaction time, s, and S_V is the MgO surface area per unit volume of reactor, m^{-1}.

The quantity S_V at a given instant of the reaction is given by

$$S_V = G_B S / V. \qquad (2)$$

Using the balance equation

$$G_B = G_B^0(1 - \eta_B) \qquad (3)$$

and introducing a function f_S that characterizes the variation in the specific surface area of the solid phase during the reaction, Eq. (2) becomes

$$S_V = G_B^0 S^0 f_S (1 - \eta_B)/V, \qquad (4)$$

where G_B^0 and G_B are the masses of MgO at the start and during the reaction, g, respectively, S^0 and S are the specific surface areas of MgO at the start and during the reaction, m^2 g^{-1}, respectively, η_B is the conversion of MgO, and the function f_S is defined as $f_S = S/S^0$.

An equation for the reaction rate per unit MgO surface area can be derived for the condition of pseudosteady state provided that some of the steps of the reaction mechanism is so slow compared to the others as to become rate-controlling. In most cases, not all the variants need to be considered; some of them can be eliminated by using a suitable experimental arrangement in the measurements, or subsequently by an assessment of the obtained kinetic data.

EXPERIMENTAL

The kinetics of the decomposition were followed by monitoring the amount of Mg^{2+} ions passing from the solid to the liquid phase. The reaction was carried out in a well-stirred isothermal batch reactor consisting of a jacketed glass vessel of cylindrical shape with an inner diameter of 6·3 cm. The suspension was stirred by passing air saturated with water vapour at the temperature of measurement through tubes extending across the lid down to the bottom of the reactor. A schematic of the apparatus is shown in Fig. 1.

The measurements were made with 200 ml of an NH$_4$Cl solution. Suspension samples with-drawn by means of a probe from the reactor in the course of the decomposition were rapidly filtered free from the solid phase and titrated in the presence of an ammonium buffer with a Chela-ton 3 solution using eriochrome black T as the indicator to determine the concentration of Mg^{2+} ions. So obtained data, the known volume of the liquid phase, and the initial amount of MgO were used to calculate the values of conversion, η_B. The measurements were carried out with chemicals of analytical grade (Lachema) and distilled water. MgO was heated before use for 8 hours at 1 200°C. Its specific surface area, as determined by the comparative dynamic method using adsorption of nitrogen from a nitrogen–hydrogen mixture at the temperature of liquid nitrogen, was 3·5 m^2 g^{-1}.

RESULTS AND DISCUSSION

Measurements performed at various flow rates of air through the reactor showed that increasing the flow rate beyond 10 litres per minute no longer accelerated the decomposition. This means that by a proper choice of experimental arrangement
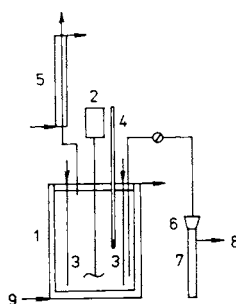

FIG. 1

Experimental set-up. 1 reactor, 2 stirrer, 3 tubes, 4 thermometer, 5 condenser, 6 sintered glass, 7 test tube, 8 vacuum pump, 9 thermostat

a condition can be attained where ammonia desorption from the suspension does not affect the reaction rate. Since all further measurements were performed under these conditions, process 4 can be discounted as the rate-controlling step. Measurements with untreated MgO and with MgO previously converted to a hydrate have shown that the prehydration has no effect on the reaction kinetics. This finding eliminates process 2 from the group of possible rate-controlling steps.

A characteristic dimension of MgO particles estimated from microphotographs at $20,000 \times$ magnification was used to calculate the specific surface area for the case of spherical shape. Good agreement of the result with the value obtained by adsorption measurements indicated that the MgO particles were not porous. This eliminates from consideration the transfer processes in the porous structure, i.e. 6b, 7a, and 8a. On the basis of the low value of the apparent activation energy, 39 kJ mol^{-1}, it may be concluded that the rate is not controlled by any of the steps of chemical nature, so that processes 1 and 3 can be excluded. Considering the mobilities of the H_3O^+, OH^-, and Mg^{2+} ions, it is reasonable to assume that neither 6a nor 7b are the slowest processes. This leaves 5 and 8b as possible rate-controlling steps.

If $Mg(OH)_2$ dissolution is considered as an elementary process, then its rate can be described by a kinetic equation of the form

$$r_{BS} = k_5(S_B - c_{Mg^{2+}}c_{OH^-}^2) \,. \tag{5}$$

Using relationships for the ionic product of water,

$$S_Z = c_{OH^-}c_{H_3O^+} \,, \tag{6}$$

and for the equilibrium constant of NH_4Cl hydrolysis,

$$K_1 = c_{NH_3}c_{H_3O^+}/(c_{NH_4^+}c_{H_2O}) \,, \tag{7}$$

the OH^- ion concentration can be expressed by

$$c_{OH^-} = S_Z c_{NH_3}/(K_1 c_{NH_4^+}c_{H_2O}) \,. \tag{8}$$

Substituting (8) in (5), we obtain

$$rr_{BS} = k_5\{S_B - c_{Mg^{2+}}[S_Z c_{NH_3}/(K_1 c_{NH_4^+}c_{H_2O})]^2\} \,, \tag{9}$$

where k_5 is the rate constant for the precipitation of $Mg(OH)_2$, mol^{-2} m^7 s^{-1}, S_B is the solubility product of $Mg(OH)_2$, mol^3 m^{-12}, c_i is the concentration of i-th component, mol m^{-3}, S_Z is the ionic product of water, mol^2 m^{-6}, and K_1 is then equilibrium constant of NH_4Cl hydrolysis.

The rate of Mg^{2+} transfer from the surface of Mg(OH)$_2$ to the bulk of the solution is described by

$$r_{BS} = k_8[(c_{Mg^{2+}})_S - c_{Mg^{2+}}], \qquad (10)$$

where k_8 is the transfer coefficient for Mg^{2+} ions, m s^{-1}, and $(c_{Mg^{2+}})_S$ is the concentration of Mg^{2+} ions at the interface, mol m^{-3}. The quantity $(c_{Mg^{2+}})_S$ can be expressed in terms of relationships for the solubility product of Mg(OH)$_2$, the ionic product of water, and the equilibrium constant of NH$_4$Cl hydrolysis. Equation (10) then takes the form

$$r_{BS} = k_8\{S_B[K_1 c_{NH_4^+} c_{H_2O}/(S_Z c_{NH_3})]^2 - c_{Mg^{2+}}\}. \qquad (11)$$

On the basis of the balance equation

$$n_B = n_B^0(1 - \eta_B), \qquad (12)$$

the reaction rate defined by Eq. (1) can be expressed as

$$r_{BV} = [G_B^0/(M_B V)] (d\eta_B/d\tau), \qquad (13)$$

where n_B^0 is the number of moles of MgO at the start of the reaction, and M_B is the molar mass of MgO, g mol^{-1}.
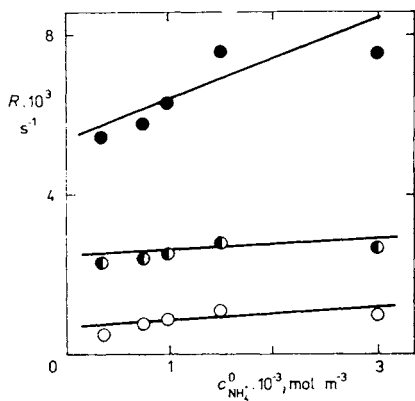

FIG. 2

A plot of $R(\equiv (d\eta_B/d\tau)_{\tau \to 0})$ against the NH$_4^+$ concentration in the starting solution at various temperatures; stoichiometric ratio of components. t, °C: ○ 50, ◐ 75, ● 100

FIG. 3

A plot of $Q(\equiv (d\eta_B/d\tau)_{\tau \to 0}/(c_{NH_4^+}^0)^2)$ against the NH$_4^+$ concentration in the starting solution at various temperatures; stoichiometric ratio of components. t, °C: ○ 50, ◐ 75, ● 100
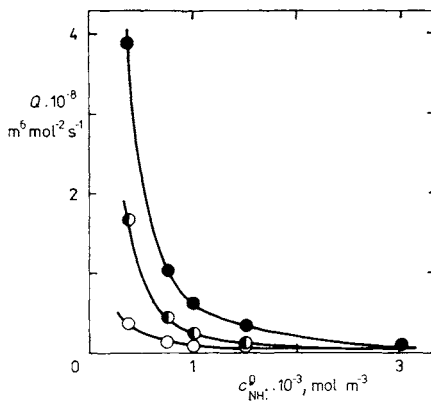
If $Mg(OH)_2$ dissolution is the rate-controlling step, then substitution of Eqs (4), (9) and (13) in (1) and rearrangement yield

$$(d\eta_B/d\tau) = k_5 M_B S^0 f_S \{S_B - c_{Mg^{2+}}[S_Z c_{NH_3}/(K_1 c_{NH_4^+} c_{H_2O})]^2\} (1 - \eta_B) . \quad (14)$$

If, on the other hand, the transfer of Mg^{2+} ions from the interface to the bulk of the solution is the rate-controlling step, then substitution of Eqs (4), (11) and (13) in (1) gives

$$(d\eta_B/d\tau) = k_8 M_B S^0 f_S \{S_B [K_1 c_{NH_4^+} c_{H_2O}/(S_Z c_{NH_3})]^2 - c_{Mg^{2+}}\} (1 - \eta_B) . \quad (15)$$

In determining which of the steps controls the rate of the decomposition reaction, it is convenient to fit experimental data to reduced forms of kinetic equations (14) and (15), which correspond to the start of the reaction. For the conditions where $c_{Mg^{2+}} \to 0$ and $\eta_B \to 0$ as $\tau \to 0$, we obtain the following equations:

for process 5

$$(d\eta_B/d\tau)_{\tau \to 0} = k_5 M_B S^0 S_B , \quad (16)$$

and for process 8b

$$(d\eta_B/d\tau)_{\tau \to 0} = k_8 M_B S^0 S_B [K_1 c_{NH_4^+}^0 c_{H_2O}/(S_Z c_{NH_3})]^2 , \quad (17)$$

where $c_{NH_4^+}^0$ is the NH_4^+ concentration in the starting solution, $mol\ m^{-3}$. In assessing which of these equations provides the better representation of the kinetic data, we used values of $(d\eta_B/d\tau)_{\tau \to 0}$ corresponding to various initial concentrations of NH_4Cl. For this purpose, experimentally obtained isotherms in η_B and τ coordinates were fitted to an empirical equation of the form

$$\ln [1/(1 - \eta_B)] = a + b\tau + c\tau^2 \quad (18)$$

and the corresponding derivatives were determined after evaluating the constants a, b, and c. Fig. 2 shows a plot of $(d\eta_B/d\tau)_{\tau \to 0}$ against the NH_4^+ concentration in the starting solution, and in Fig. 3 the ratio of the derivative to the square of NH_4^+ concentration in the starting solution is plotted as a function of NH_4^+ concentration in the starting solution. As indicated by kinetic equations (16) and (17), the two quantities should be independent of the concentration. Comparison of Figs 2 and 3 shows that this requirement is better satisfied by Eq. (16). The observed slightly increasing trend in the values of $(d\eta_B/d\tau)_{\tau \to 0}$ with increasing concentration may be ascribed to changes in the solubility product of $Mg(OH)_2$. Thus we may conclude that the slowest, and hence the rate-controlling step of the decomposition reaction under study is the dissolution of the solid phase.

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